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THERMODYNAMIC PROPERTIES OF CARBON-DIOXIDE AND NITROGEN

MIXTURES BEHIND A NORMAL SHOCK WAVE

By Henry T. Woodward

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THERMODYNAMIC PROPERTIES OF CARBON-DIOXIDE AND NITROGEN

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SUMMARY

Thermodynamic properties of the gas in equilibrium behind normal shock waves in mixtures of carbon dioxide and nitrogen are calculated for resulting temperatures from 3000° to 8000° K at intervals of 1000° K and pressures of 1, 10, and 100 atmospheres. Equilibrium temperature, pressure, density, and component mole fractions are presented as functions of shock velocity and ambient pressure for an initial temperature of 300° K. Mixtures of 25, 50, and 75 percent N_2 by volume are considered. The amounts of NO, C, and CN which are formed could make a significant contribution to the electron density and the radiative heat flux potential.

INTRODUCTION

Successful flight through an atmosphere depends on knowledge of thermodynamic and transport properties of the atmosphere. Now that exploration of other planets is being contemplated, there is increasing interest in the properties of their atmospheres, especially the shock-heated gases in front of space vehicles entering these atmospheres at high velocities.

Theoretical calculations that predict gas properties behind a shock wave are based on knowledge of the proportions of the constituent gases in the ambient atmosphere. These proportions can be accurately measured in our own atmosphere, but precise information about other planetary atmospheres is lacking. Such calculations must therefore be based on assumed proportions of gases in these atmospheres. Likely components of the atmospheres of Mars and Venus include carbon dioxide and nitrogen (ref. 1).

Equilibrium properties of gases whose ambient composition is 100 percent ${\rm CO_2}$, 98.1 percent ${\rm N_2}$ and 1.9 percent ${\rm CO_2}$, and 100 percent ${\rm N_2}$ are given in references 2, 3, and 4, respectively. In the present report, ambient atmospheres with the following compositions are assumed.

Case	Percent composition by volume			
	CO ₂	N_2		
I	25	75		
II	50	50		
III	75	25		

A few additional cases are considered in order to make curve fairing more precise. Properties in the shocked gases are calculated for equilibrium temperatures and pressures ranging from 3000° to 8000° K and 1 to 100 atmospheres. These properties are presented for corresponding velocities from 10,000 to 26,000 feet per second and ambient pressures of 0.01, 0.1, and 1.0 atmosphere as obtained through the normal shock conservation equations.

PROCEDURE

When the ambient gas is heated and compressed to various temperatures and pressures behind a shock wave, the composition of the gas changes. The first task is to determine the proportions of the components of this gas as a function of temperature and pressure, since these are necessary to calculate other gas properties.

The significant components present in the range of equilibrium temperatures and pressures of interest can be estimated from the magnitudes of the equilibrium constants of possible chemical reactions. The equilibrium constant for a reaction is

$$K_{P} = \exp\left(-\frac{\Delta F^{O}}{RT_{2}}\right) \tag{1}$$

where ΔF^O is the standard free energy change of the reaction at equilibrium temperature T_2 , and R is the universal gas constant. Ideal-gas free-energy values for possible components are tabulated or can be calculated for various temperatures as shown in reference 5. In this case it was estimated that the significant components are gas phases of CO_2 , N_2 , CO, O_2 , O, C, N, NO, and CN. Determining the proportions of these nine components requires the solution of nine equations in these nine unknowns - one equation expressing Dalton's law of partial pressures, six equations expressing the law of mass action for six independent reactions involving these components, and two material balance equations.

Dalton's law of partial pressures states that the sum of the partial pressures of the components is equal to the total pressure of the mixture. In this case it follows that

$$X_{CO_2} + X_{N_2} + X_{CO} + X_{O_2} + X_{O} + X_{C} + X_{N} + X_{NO} + X_{CN} = 1$$
 (2)

where $X_{\rm CO_2}$, for example, is the ratio of the number of particles of ${\rm CO_2}$ to the total number of particles in the mixture.

The six independent reactions and the corresponding applications of the law of mass action are

$$\frac{(x_{CO})(x_{O_2})^{1/2}}{x_{CO_2}} = \frac{KP_1}{P_2^{1/2}}$$
(3)

$$CO \neq C + O$$

$$\frac{(X_C)(X_O)}{X_{CO}} = \frac{K_{P_2}}{P_2}$$
 (4)

$$0_2 \neq 20$$

$$\frac{(x_0)^2}{x_{0_2}} = \frac{K_{P_3}}{P_2}$$
 (5)

$$\frac{\left(x_{N}\right)^{2}}{x_{N_{2}}} = \frac{K_{P_{4}}}{P_{2}} \tag{6}$$

$$NO \neq \frac{1}{2} N_2 + \frac{1}{2} O_2 \frac{(X_{N_2})^{1/2}(X_{O_2})^{1/2}}{X_{NO}} = K_{P_5}$$
 (7)

$$\frac{(\mathbf{x}_{C})(\mathbf{x}_{N})}{\mathbf{x}_{CN}} = \frac{\kappa_{P_{\mathbf{G}}}}{P_{2}}$$
(8)

where P_2 is the total equilibrium pressure in atmospheres and the values of $K_{\mbox{\scriptsize P}}$ are calculated from equation (1).

The two material-balance equations state that the proportions of carbon, oxygen, and nitrogen particles in molecular and atomic forms are the same in the

shocked gas as they are in the ambient gas. The ratio of oxygen particles to carbon particles is 2, and the ratios of nitrogen particles to carbon particles are 6, 2, and 2/3 for cases I, II, and III, respectively. These relationships can be expressed as

$$\frac{2X_{O_2} + X_{NO} + 2X_{CO_2} + X_{CO} + X_{O}}{X_{CO_2} + X_{CO} + X_{CN} + X_{C}} = 2 \text{ for cases I, II,}$$
(9)

$$\frac{2X_{N_2} + X_{NO} + X_N + X_{CN}}{X_{CO_2} + X_{CO} + X_{CN} + X_C} = \begin{cases} 6 \text{ for case I} \\ 2 \text{ for case II} \\ 2/3 \text{ for case III} \end{cases}$$
 (10)

Equations (2) through (10) are combined, simplified, and solved for $\, X \,$ by a systematic iterative procedure. These component proportions are listed for corresponding equilibrium temperatures and pressures in table I.

Once these component proportions are known, other gas properties can be calculated. The molecular weight of the mixture is

$$M_2 = \sum_{i} X_{i}M_{i} \tag{11}$$

where M_i is the molecular weight of component i.

From the equation of state, the density of the mixture is then

$$\rho_2 = \frac{P_2}{\frac{R}{M_2} T_2} \tag{12}$$

Densities are also listed in table I.

The energy of the mixture per original mole of ambient gas is

$$E_2 = \frac{M_1}{M_2} \sum_{i} X_{i} E_{i}$$
 (13)

where $E_{\rm i}$ includes the translational, internal, and formation energy per mole of component i obtained from reference 5; $M_{\rm l}$ is the molecular weight of the ambient gas, given by

$$M_{1} = X_{CO_{2}}M_{CO_{2}} + X_{N_{2}}M_{N_{2}}$$
 (14)

where X_{CO_2} and X_{N_2} are the assumed ambient proportions of CO_2 and N_2 .

When the density and energy have been determined, the velocity and ambient pressure which give rise to the equilibrium properties behind a normal shock wave can be calculated.

The equations expressing the conservation of mass, momentum, and energy across a normal shock wave are

$$\rho_1 V_1 = \rho_2 V_2 \tag{15}$$

$$P_1 + \rho_1 V_1^2 = P_2 + \rho_2 V_2^2 \tag{16}$$

$$E_1 + \frac{P_1}{\rho_1} + \frac{1}{2} V_1^2 = E_2 + \frac{P_2}{\rho_2} + \frac{1}{2} V_2^2$$
 (17)

where subscript 1 designates properties ahead of the shock and subscript 2 designates properties behind the shock.

The energy per mole of ambient gas at 300° K is

$$E_1 = X_{CO_2} E_{CO_2} + X_{N_2} E_{N_2}$$
 (18)

where $E_{\rm CO_2}$ and $E_{\rm N_2}$ are the energies per mole of ${\rm CO_2}$ and ${\rm N_2}$ at ${\rm 300}^{\circ}$ K obtained from reference 6. For a given T_2 , P_2 , P_2 , E_2 , and E_1 the normal shock equations are solved by the method of reference 7 for the corresponding normal shock velocity V_1 and ambient pressure P_1 . The results of curve fairing and crossplotting of these points are shown in figures 1, 2, 3, and 4, where equilibrium temperature, pressure, density, and component gas fractions behind a normal shock wave are given for corresponding values of velocity and ambient pressure.

DISCUSSION

According to the study made in reference 3 of parameters associated with entry into an assumed Martian atmosphere (98.1 percent N_2 and 1.9 percent CO_2), the proportions of NO, C, and CN are of special interest. This study shows that a large radiative heat flux potential exists primarily because of the presence of CN. It also shows that because of their relatively low ionization potentials, NO and C can contribute significantly to the electron density concentrations at relatively low temperatures.

As the velocity (i.e., equilibrium temperature) increases, the proportion of NO reaches a maximum of as much as 6 percent and decreases before the proportions of C and CN show a significant increase, as shown in figure 4. The effect of ambient proportions of $\rm CO_2$ and $\rm N_2$ is shown in figure 5 for a velocity of 20,000 ft/sec and ambient pressure of 0.01 atmosphere. The proportion of NO

reaches a maximum when the ambient N_2 proportion is about 30 percent, whereas the maximum C and CN proportions occur at an ambient N_2 proportion of about 85 percent.

In figure 6, the proportion of CN is shown as a function of the ambient proportion of N_2 for a temperature of 6000° K and pressures of 1 and 10 atmospheres. Values obtained from reference 3 are also plotted.

The heat flux potential also increases with increasing temperature. Figure 1 shows the equilibrium temperature as a function of velocity and figure 7 shows that the equilibrium temperature increases with increasing ambient proportion of N_2 . Since radiative heating is extremely sensitive to temperature, this latter effect may be important.

Ames Research Center
National Aeronautics and Space Administration
Moffett Field, Calif., Nov. 26, 1962

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TABLE I.- COMPONENT MOLE FRACTIONS AND DENSITY

(a) Case I

ρ2, lb/ft3	7.461_3 7.743_2 7.918_1	4.998_3 5.238_2 5.509_1	3.874_3 3.964_2 4.129_1	2.964 <u>.</u> 3 3.181 <u>.</u> 2 3.310 <u>-</u> 1	1.975_3 2.457_2 2.717_1	1.431_3 1.744_2 2.166_1
CN	3.909_9	2.004_6	1.774-4	3.340 <u>.</u> 3	7.549 ₋₃	2,798_3
	3.042_9	1.113_6	6.631 ₋₅	1.361 <u>.</u> 3	8.720 ₋₃	1.265_3
	2.346_	8.410_7	3.351 ₋₅	5.551 <u>.</u> 4	4.398 ₋₃	1.521_2
G	1.152_ 12.778_ 6.688_ 1.3	1.660_7 2.868_8 6.692_9	1.049_4 1.226_5 1.937_8	8.021_3 9.472_4 1.190_4	6.788_2 1.715_2 2.428_3	1.051_1 6.902_2 1.852_2
NO	2.254_2	2.447_2	1.037_2	4.720_3	2.209_3	6.951_4
	1.896_2	4.362_2	2.883_2	1.557_2	9.060_3	4.686_3
	1.404_2	5.018_2	5.791_2	4.180_2	2.841_2	1.831_2
0	2.531_2	1.562 ₋₁	1.872_1	1.890_1	2.151_1	2.247_1
	6.598_3	8.657 ₋₂	1.627_1	1.808_1	1.929_1	2.200_1
	1.525_3	3.076 ₋₂	1.022_1	1.495_1	1.698_1	1.917_1
N	1.146_5 3.697_e 1.184_e	1.375_3 4.422_4 1.432_4	2.516_2 8.047_3 2.574_3	1.600_1 5.519_2 1.792_2		6.128 4.218 1.891
CO	1.368_1	2.009_1	1.983_1	1.712_1	6.649_2	9.573 ₋₃
	8.600_2	1.924_1	2.015_1	1.934_1	1.506_1	6.155 ₋₂
	4.785_2	1.595_1	1.999_1	2.009_1	1.877_1	1.439 ₋₁
C02	9.247_2	4.267_3	2.174_4	2.483_5	3.063_8	1.780_7
	1.524_1	2.265_2	1.919_3	2.683_4	6.223_5	1.121_5
	1.960_1	6.670_2	1.196_2	2.304_3	6.826_4	2.284_4
02	4.446_2	1.013_2	6.694_4	8.763_5	2.540_5	9.118
	3.022_2	3.111_2	5.057_3	8.018_4	2.043_4	8.744
	1.614_2	3.928_2	1.995_2	5.481_3	1.583_3	6.640
N ₂	6.779_1	6.026 ₋₁	5.786 ₋₁	4.636_1	2.010_1	4.433_2
	7.058_1	6.232 ₋₁	5.919 ₋₁	5.517_1	4.202_1	2.101_1
	7.245_1	6.534 ₋₁	6.055 ₋₁	5.815_1	5.334_1	4.223_1
P2, atm	1 10 100	1 10 100	1 10 100	1 10 100	1 10 100	1 10 100
^д г,	3000	0001	5000	0009	7000	8000

places to the Note: A group of digits followed by -n indicates that the decimal point should be n left of the first digit.

TABLE I.- COMPONENT MOLE FRACTIONS AND DENSITY - Continued

(b) Case II

ρ ₂ , 1b/ft ³	7.945_3 8.465_2 8.783_1			l .	1.964_3 2.376_2 2.594_1	1.437_3 1.723_2 2.094_1
CN	3.717.9 2.911.9 2.214.9		1.304_4 4.895_5 2.626_5	2.568_3 9.996_4 4.030_4	7.186_3 7.073_3 3.247_3	2.960_3 1.228_2 1.265_2
ວ	1.387_11 3.317_12 7.811_13		1.041_4 1.223_5 2.035_6	8.417_3 9.440_4 1.176_4	9.402_2 1.916_2 2.448_3	1.786_1 9.791_2 2.131_2
NO	2.435_2	2.986_2	1.297_2	5.786_3	2.467_3	7.524 <u>4</u>
	2.034_2	5.049_2	3.601_2	1.952_2	1.083_2	5.188 <u>3</u>
	1.512_2	5.623_2	6.999_2	5.270_2	3.555_2	2.164_2
0	3.462_2	2.553_1	3.160_1	3.163_1	3.495_1	3.906_1
	8.830_3	1.319_1	2.747_1	3.074_1	3.176_1	3.560_1
	2.032_3	4.434_2	1.655_1	2.563_1	2.903_1	3.138_1
N	9.046_6 2.963_6 9.571_7	1	1.863_2 5.953_3 1.920_3	1.172_1 4.068_2 1.317_2	3.022_1 1.460_1 5.244_2	3.816_1 2.887_1 1.366_1
CO	2.254_1	3.393_1	3.323_1	3.006 ₋₁	1.496_1	2.828_2
	1.374_1	3.267_1	3.394_1	3.276 ₋₁	2.771_1	1.413_1
	7.447_2	2.638_1	3.401_1	3.402 ₋₁	3.237_1	2.711_1
COS	2.096_1	1.178_2	6.150_4	7.295_5	1.120_5	9.140_7
	3.260_1	5.857_2	5.461_3	7.729_4	1.885_4	4.162_5
	4.064_1	1.591_1	3.296_2	6.692_3	2.012_3	7.042_4
02	8.321_2	2.706_2	1.908_3	2.454_4	6.705_s	2.755_s
	5.413_2	7.218_2	1.442_2	2.318_3	5.538_4	2.289_4
	2.866_2	8.163_2	5.234_2	1.612_2	4.626_3	1.779_3
Nz	4.228	3.356_1	3.173_1	2.489_1	9.492_2	1.719_2
	4.533 ₁	3.599_1	3.240_1	2.998_1	2.215_1	9.841_2
	4.733 ₁	3.948_1	3.371_1	3.143_1	2.858_1	2.203_1
P2, atm	1 10	1 10	1 10 100	1 1.0 1.00	1 10 100	1 10
T2, °K	3000	7,000	5000	0009	7 000	8000

TABLE I.- COMPONENT MOLE FRACTIONS AND DENSITY - Concluded (c) Case III

ρ2, lb/ft ³	8.435_3 9.189_2 9.650_1	4.680_3 5.345_2 6.089_1	3.491_3 3.643_2 4.075_1	2.774_3 2.897_2 3.066_1 2.001_3 2.333_2 2.502_1	1.462_3 1.745_2 2.055_1
CN	2.812_9 2.218_9 1.676_9	1.016_6 6.534_7 5.366_7	8.323_5 3.095_5 1.705_5	1.626_3 6.279_4 2.477_4 4.638_3 4.502_3 1.995_3	1.865_3 8.019_3 8.062_3
ນ	1.534_11 3.643_12 8.449_13	1.739_7 3.377_8 8.205_9	1.031_4 1.209_5 2.066_6	8.541_3 9.322_4 1.147_4 1.103_1 1.993_2 2.407_3	2,360_1 1,166_1 2,241_2
NO	1.981_2 1.668_2 1.254_2		1.089_2 3.018_2 5.781_2	4.734-3 1.633-2 4.416-2 1.778-3 8.675-3 2.958-2	4.826_4 3.709_3 1.718_2
0	4.116-2 1.044-2 2.409-3		4.119_1 3.599_1 2.138_1	4.146-1 4.042-1 3.409-1 4.580-1 4.159-1 3.864-1	5.255 ₋₁ 4.640 ₋₁ 4.109 ₋₁
N	6.191_6 2.055_6 6.695_7			7.316_2 2.588_2 8.299_3 1.662_1 8.931_2 3.278_2	1.819_1 1.584_1 8.282_2
CO	2.961_1 1.785_1 9.549_2		1		
C02	3.274_1 5.006_1 6.178_1	1.967 9.629 2.549	1.034_3 9.262_3 5.586_2	1.272_4 1.319_3 1.155_2 2.258_5 3.363_4 3.505_3	2.186 8.419_5 1.269_3
20	1.176_1 7.569_2 4.027_2	4.457 1.123 1.224	3.241_3 2.475_2 8.732_2	4.217 4.007 2.852 1.152 9.496 8.196	4.987 3.888 3.050
N2	1.979_1 2.181_ 2.315_1	1.410 1.548 1.770 1.770 1.	1.319_1 1.326_1 1.378_1	9.695_2 1.213_1 1.248_1 2.871_2 8.287_2 1.116_1	3.908_3 2.961_2 8.098_2
P2, atm	1 10 100	1 100 100	1 10 100	100 100 100 100	10 100
T2, oK	3000	1,000	5000	7000	8000

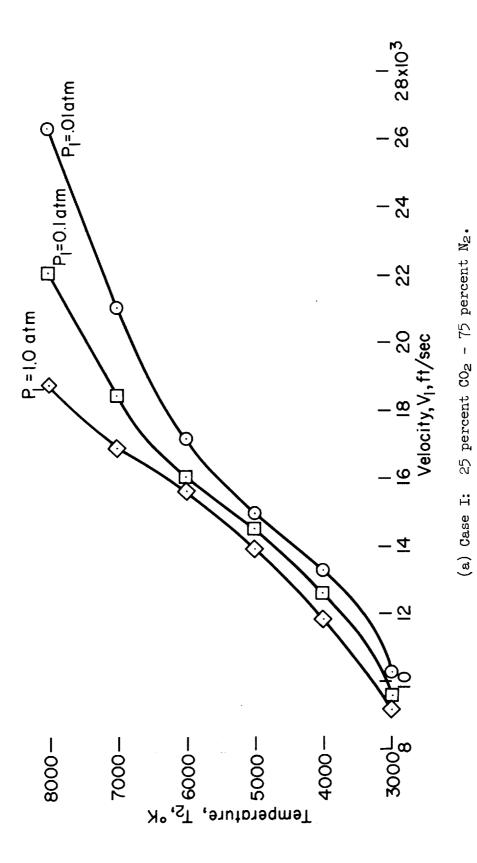
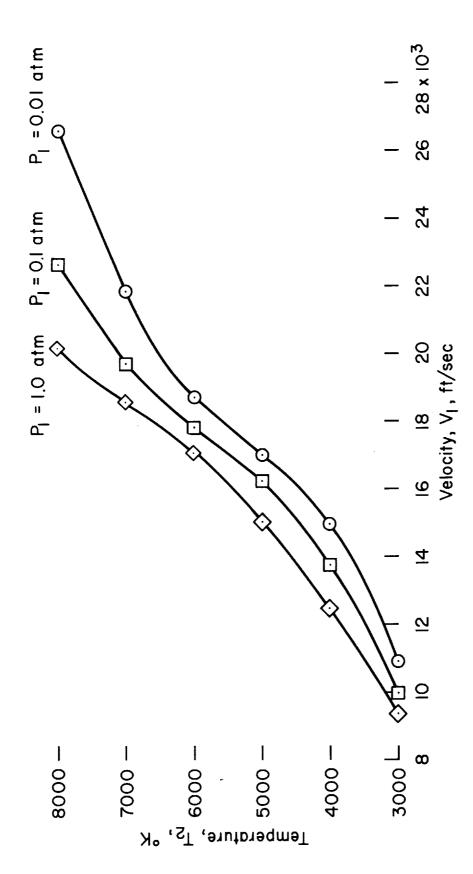
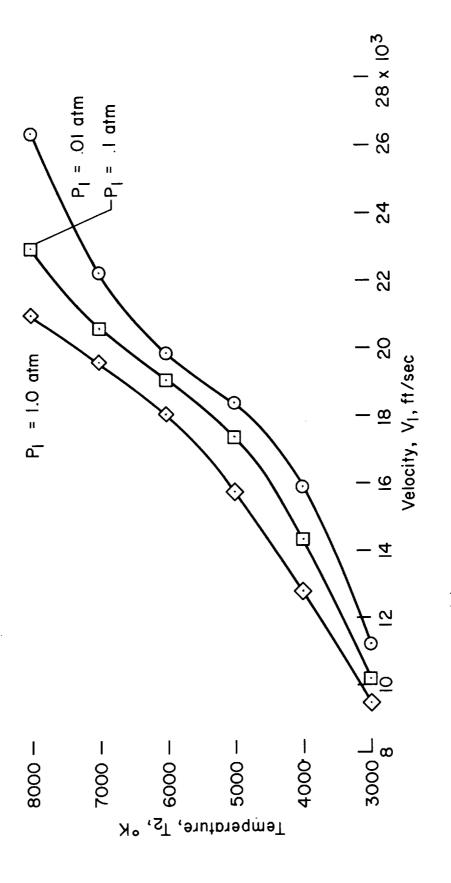


Figure 1.- Temperature as a function of normal shock velocity.



(b) Case II: 50 percent ${\rm CO_2}$ - 50 percent ${\rm N_2}$.

Figure 1.- Continued.



(c) Case III: 75 percent CO2 - 25 percent Nz. Figure 1.- Concluded.

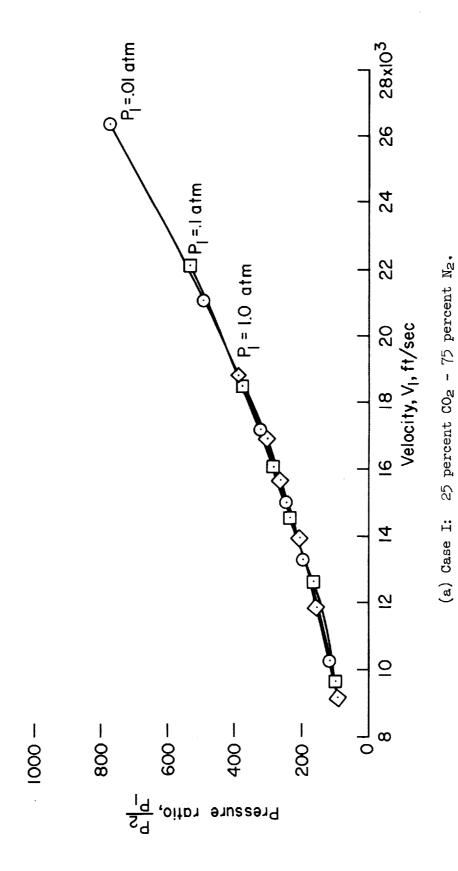


Figure 2.- Pressure ratio as a function of normal shock velocity.

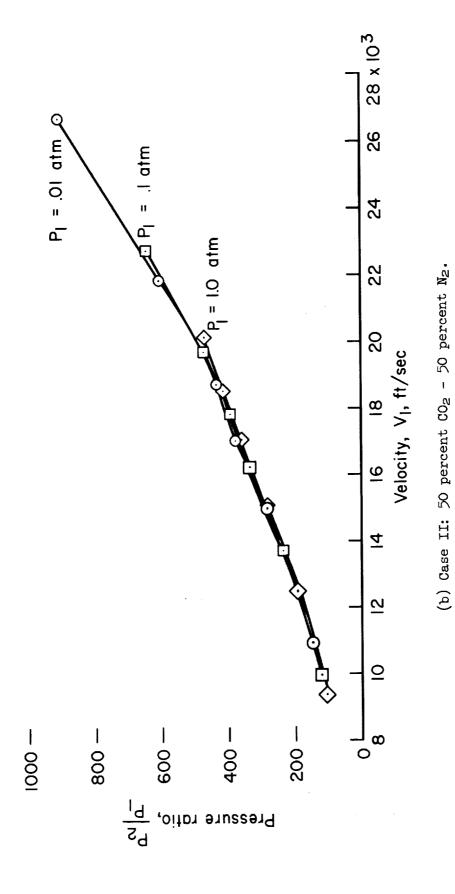


Figure 2.- Continued.

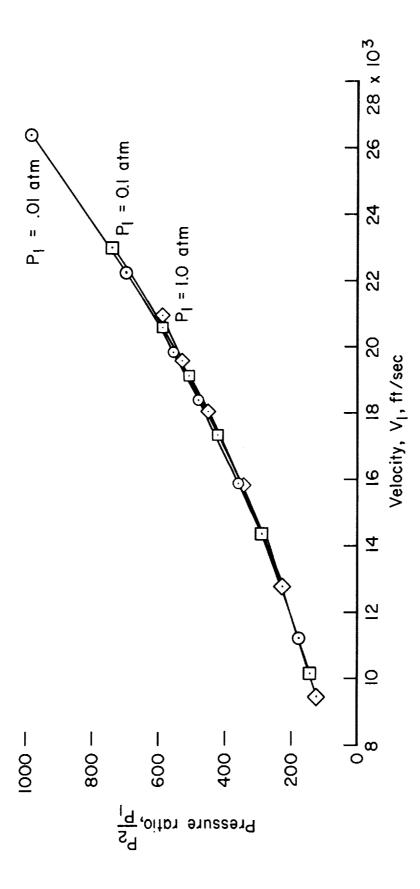
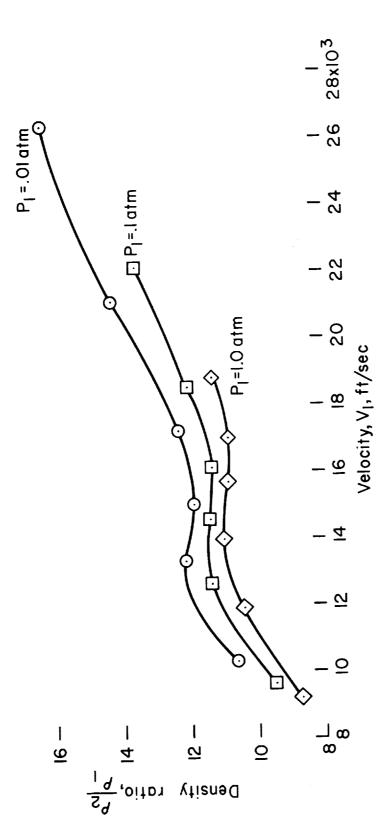


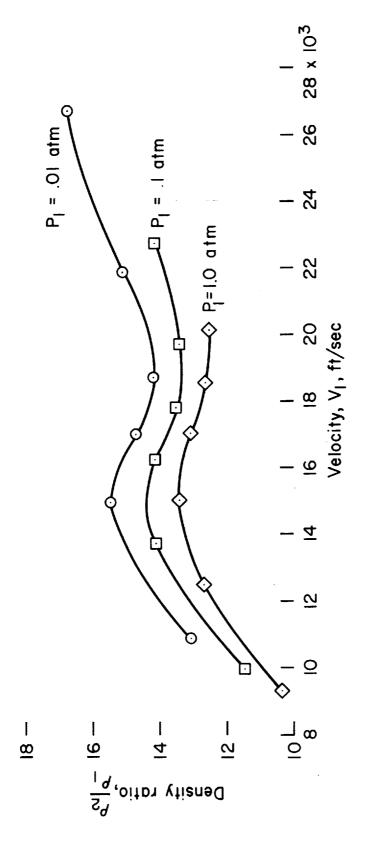
Figure 2. - Concluded.

(c) Case III: 75 percent ${\rm CO_2}$ - 25 percent ${\rm N_2}$.



(a) Case I: 25 percent CO₂ - 75 percent N₂. Figure 3.- Density ratio as a function of normal shock velocity.

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(b) Case II: 50 percent ${\rm CO_2}$ - 50 percent ${\rm N_2}$.

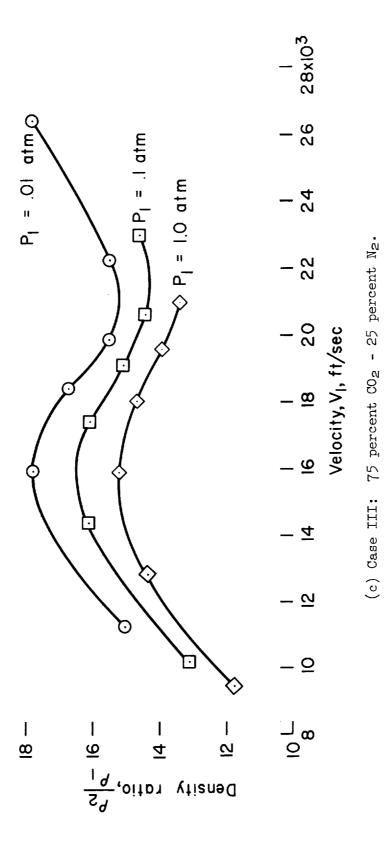
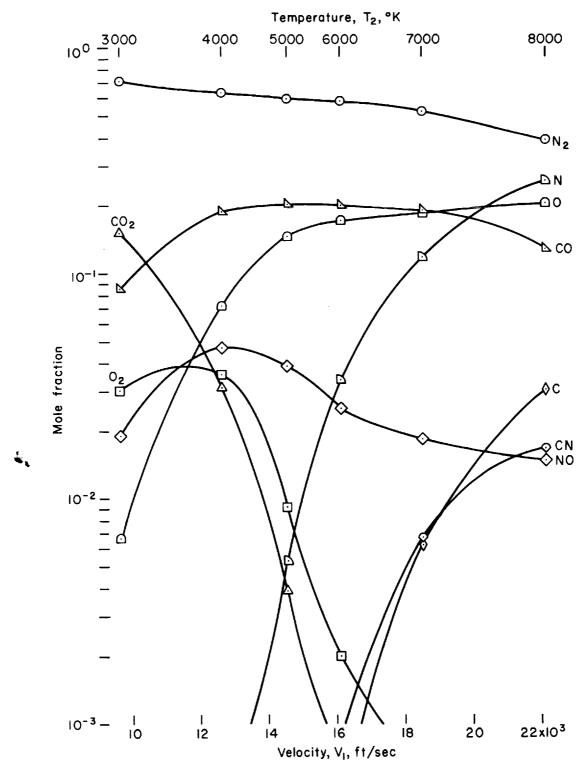
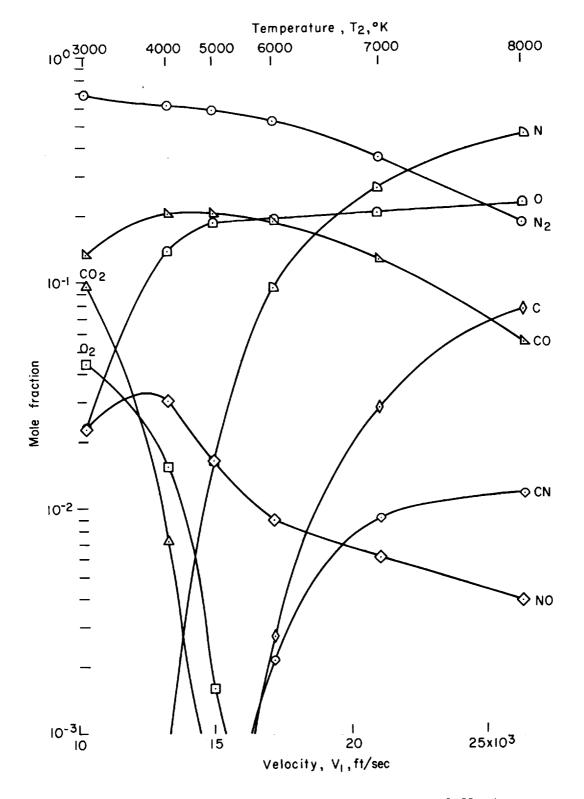


Figure 3.- Concluded.

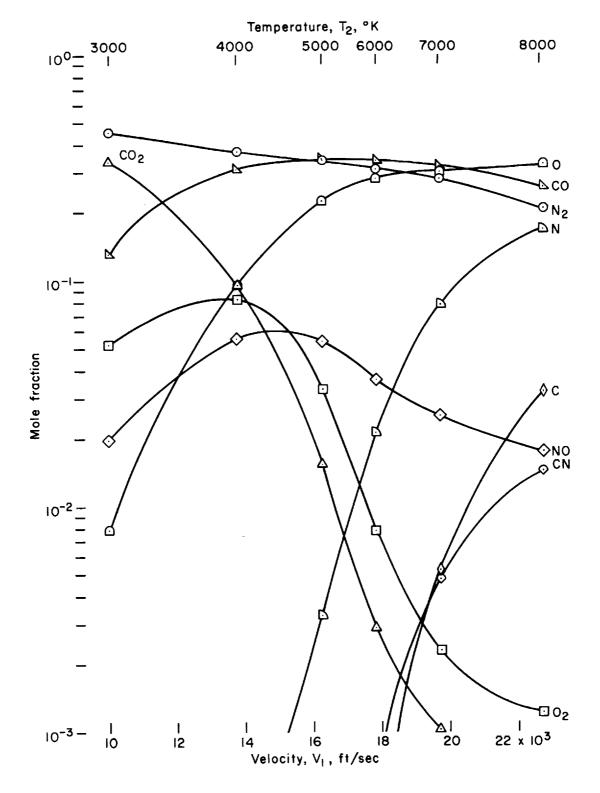


(a) Case I: 25 percent CO_2 - 75 percent N_2 ; P_1 = 0.1 atm.

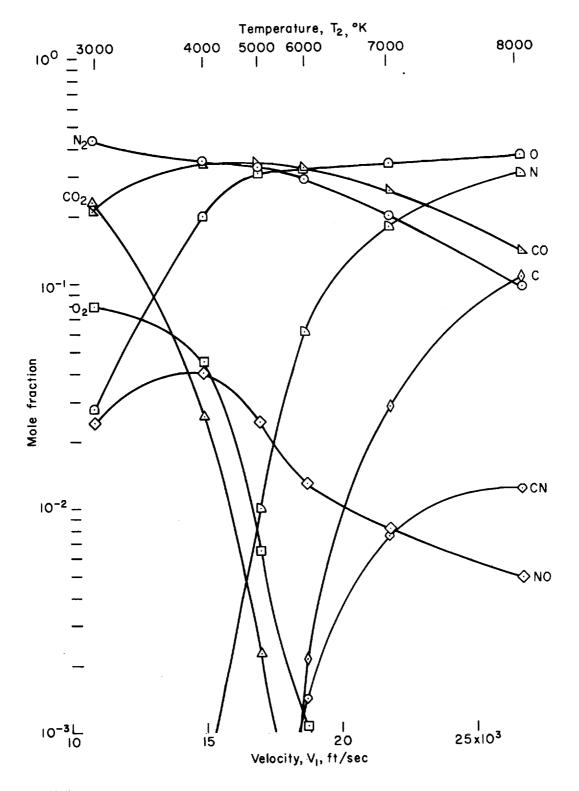
Figure 4.- Component mole fractions as a function of normal shock velocity.



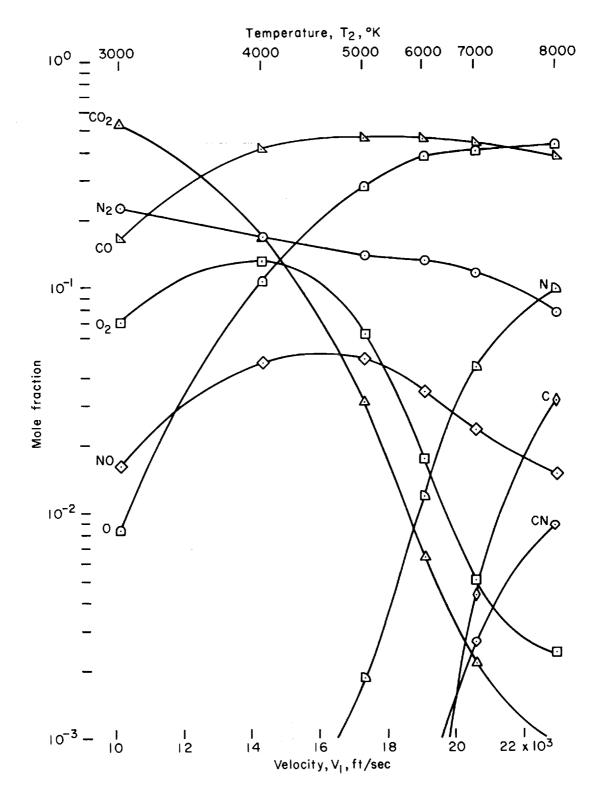
(b) Case I: 25 percent CO_2 - 75 percent N_2 ; P_1 = 0.01 atm. Figure 4.- Continued.



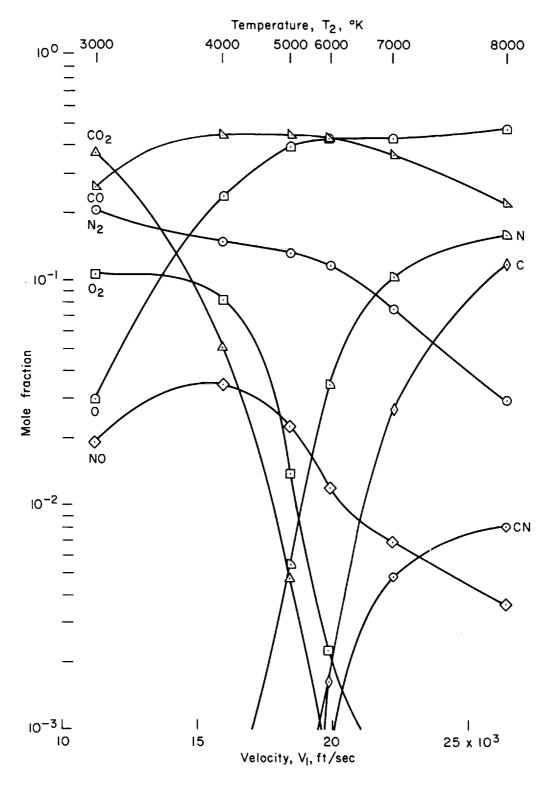
(c) Case II: 50 percent CO_2 - 50 percent N_2 ; P_1 = 0.1 atm. Figure 4.- Continued.



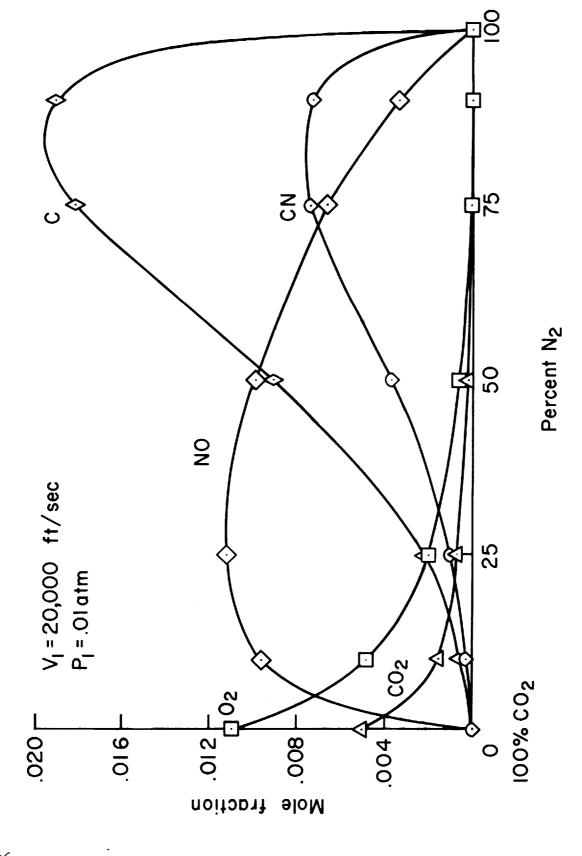
(d) Case II: 50 percent CO_2 - 50 percent N_2 ; P_1 = 0.01 atm. Figure 4.- Continued.



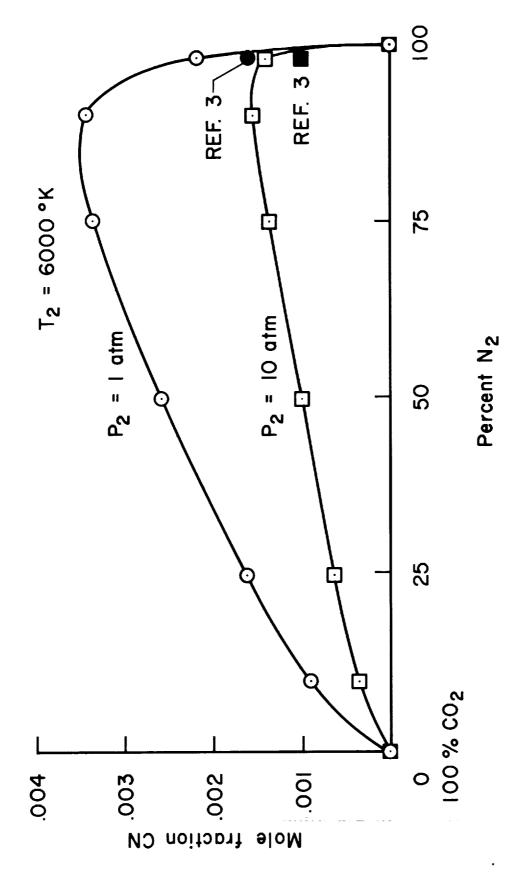
(e) Case III: 75 percent CO_2 - 25 percent N_2 ; P_1 = 0.1 atm. Figure 4.- Continued.



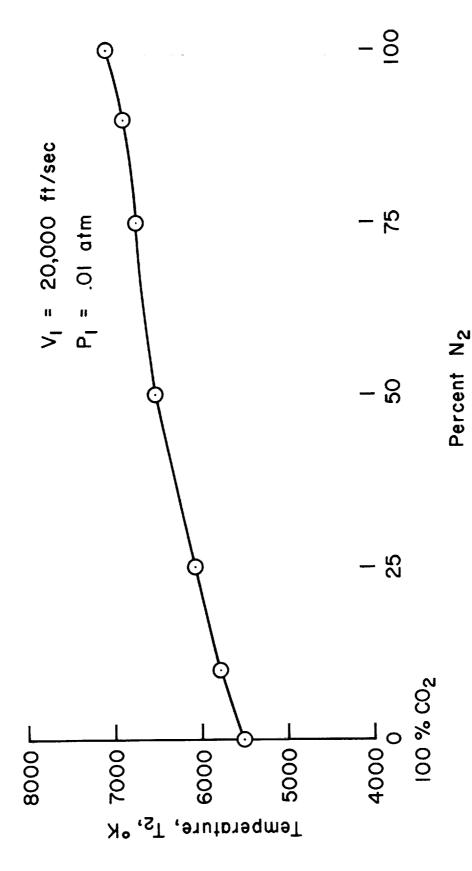
(f) Case III: 75 percent CO_2 - 25 percent N_2 ; P_1 = 0.01 atm. Figure 4.- Concluded.



N2 Figure 5.- Mole fractions as a function of ambient mole fraction of



 $^{
m N2}$ as a function of ambient mole fraction of CN Figure 6.- Mole fraction of



 \mathbb{N}_{2} Figure 7.- Temperature as a function of ambient mole fraction of